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Metals percentage effect in flame retardants industry

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Abstract

The highly demand of delaying systems in both civilian as space industry and military as fuses forces the researcher to initiate different research interested area. The common compositions for gasless delay compositions was tungsten (W) fuel modified polyvinyl acetate (PVA), $BaCrO_4$, $KClO_4$. The compositions are fabricated and loaded in delay containers. This research demonstrated the effect of varying the fuels (W) using both theoretical and experimental methods. Using the ICT code to predict the performance of the compositions and using the central testing unit for burning measurements. As the fuel percentage increase from (25% to 45%) decreasing in both oxygen and heat of formation is the main theoretical result for increasing fuel percentage. The decay of burning rate as the percentage of fuel increase have also been measured. Different characterization test like sensitivity tests and thermal analysis also have been done. all results revealed that compositions are very safe and reliable during manufacturing and usage.

Keywords: Tungsten; Thermal analysis; ICT code.

1- Introduction

The energetic materials which plays the timing events are very important in both civil and military industries. The illuminating signals shouted by hand as an example uses the delay elements for ejecting the illuminating cartridge [1]. In the same importance the delay elements have an important role for controlling the blasting sequence in all mining operations and judge the environmental effect for explosive charge [2]. The energetic materials composition used in delays composed from metals and different oxidizers which are the main ingredients and other additives are used for producing special desirable effects [3].

The black powder was used as a delay element since World War and continue used for different industrial and military purpose. Different researcher study advances gassy timing delay compositions which are composed of different constituents as Al and Si/Bi_2O_3/Sb_2O_3 [4,5]. Compositions based on red phosphorus and different metal oxide with nano particles are very candidate to be used in different application [6].

Black powder delays are constructed in a manner having intermediate layer with percentage of (55-75) potassium nitrate, small percentage of charcoal from 5 to 20 and the residue from sulfur [7].

The ignition train of black powder start by burning the intermediate core with uniform time till it delivers the ignition to detonator. Other compositions systems based on fluoropolymer-are suggested to work as the black powder [8]. limitation of using black powder in different applications due to the main feature of liberation of large volume of gases [9].

Advanced industrial products which need to be with high performance and low environmental impact led to replacement the gassy delays with gasless timing systems. Gasless delay systems produce small amount of gases but it still safe and reliable than other gassy systems [10].

The main components of pyrotechnics reactions are (fuels) as magnesium, aluminum, tungsten or nonmetals like carbon, sulfur, and polymeric binder for storing and safety [11]. Different types of Oxidizers are usually nitrates or perchlorates, have been used for uniform burning along the delay elements ignitions [12]. Constituents for most commonly timing energetic systems were oxidizers as perchlorate, burning modifier as chromate and fuels as tungsten [13].

This research investigates the effect of the percentage of fuels on delay performance and demonstrate different parameter as oxygen balance heat of formation and other relations.

2- Theoretical Calculations

Thermochemical program named ICT was used for calculation the main parameter which used for prediction the performance of delays. To study the effect of the weight percentage of fuel on the performance of delay compositions five different compositions were prepared as given in tables (1).

Table 1. Formulation of delay compositions based on different fuel percentage

Ingredients Wt.%	S1	S2	S3	S4	S5
W	45	40	35	30	25
$BaCrO_4$	35	35	35	35	35
$KClO_4$	10	15	20	25	30
PVA	10	10	10	10	10

At constant burning rate modifier $BaCrO_4$ / binder ratio. It is clear from figures (1-3) that the density, oxygen balance and heat of formation of the delay formulations changes by using different percentage of fuel (W) with respect to oxidizer ($KClO_4$) at constant binder/burning rate modifier ratio.

Delay compositions heat of formation decreases as the percentage of fuel (W) increase is assumed to relay on the heat of formation of oxidizer ($KClO_4$) which is much higher compared to that of fuel.

The sharp decrease of oxygen balance percentage form (-5.34% to -18.06%) as the fuel percentage increase from (25% to 45%) this is because the slight increase in number of moles of fuel (W) from (1.359 to 2.447 mole) in summary formula for reactants heavily impacted that of oxygen from (16.45 to 10.68 mole) so the mixture become more fuel rich. The higher density of W (19.3 g/cm^3) compared to that $KClO_4$ (4.8 g/cm^3) is the reason

Nile Journal of Basic Science

Volume 3, Number 1, October 2023

Journal Webpage: https://njbs.journals.ekb.eg

why the mixture density values increase from (3.473 to 4.569 g/cm^3) with the increase of fuel percentage from (25% to 45%).

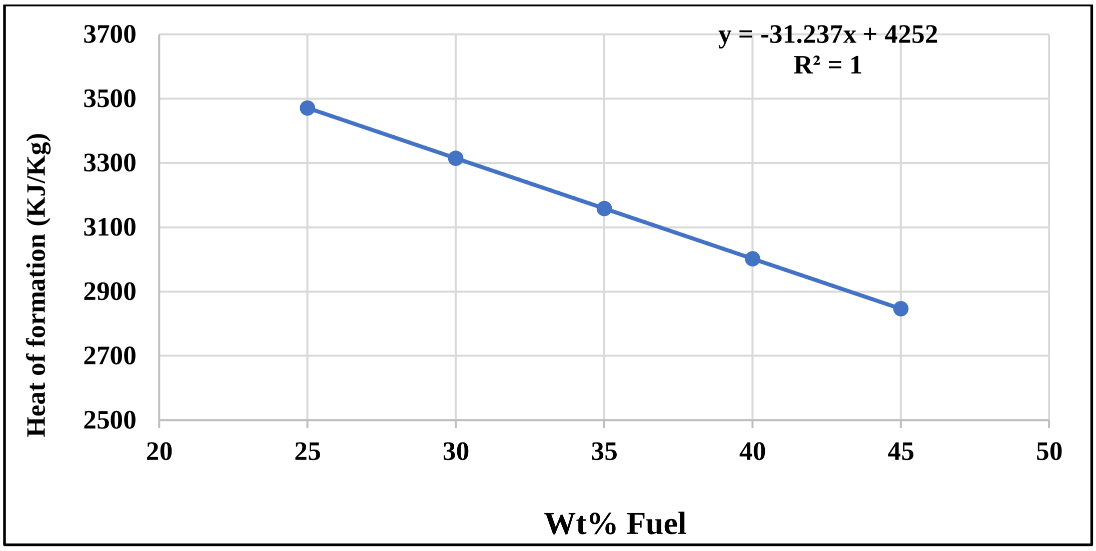

Figure 1. Relation between heat of formation and percentage of fuel (W).

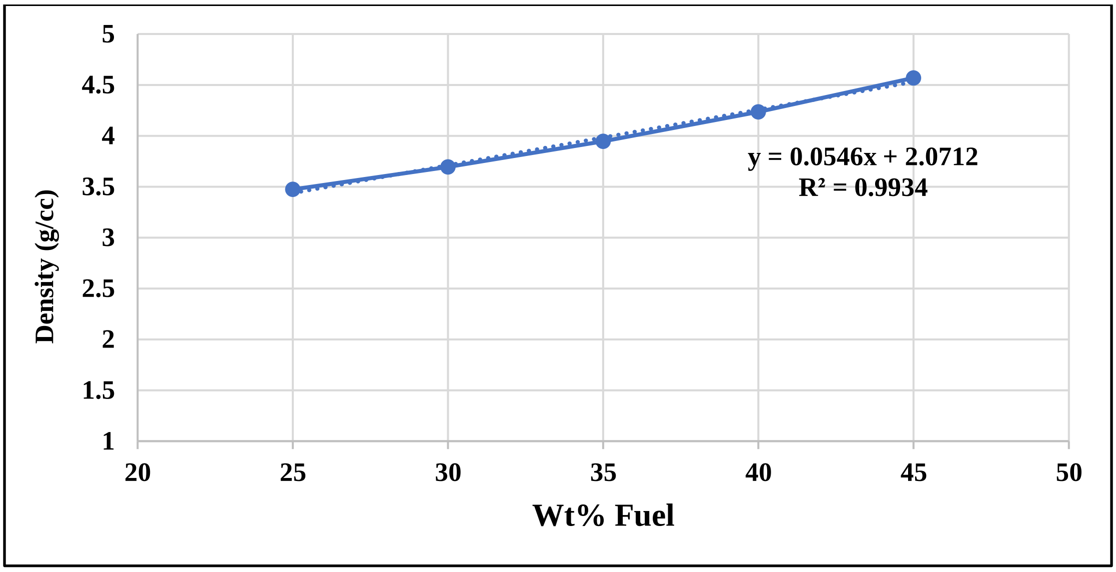

Figure 2. Relation between density and percentage of fuel (W).

Nile Journal of Basic Science

Volume 3, Number 1, October 2023

Journal Webpage: https://njbs.journals.ekb.eg

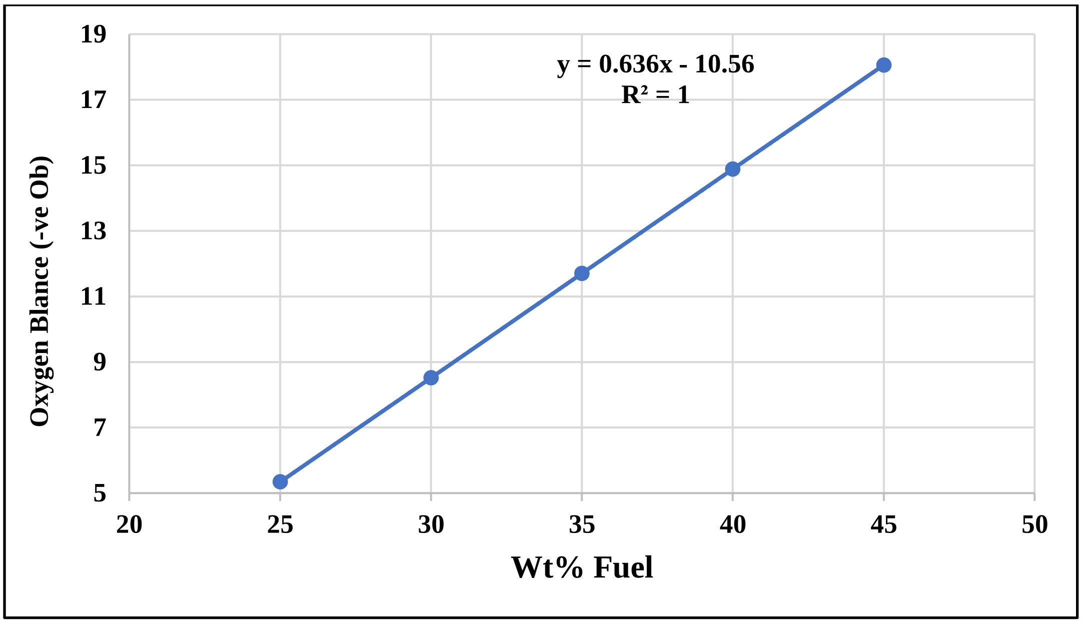

Figure 3. Relation between oxygen balance and percentage of fuel (W).

3- Experimental Part

3.1. Preparations procedure

All the materials used were supplied by Kaha Company and Abu Zaabal company for specialist industries. The selected chemicals are safe in handling and reliable the preparation procedures as in figure (4) for gasless delay compositions can be described as follows:

1. The required percentage of fuel, burning rate modifier and oxidizer was mechanically mixed.
2. Preparation of the binder liquor through dissolving in acetone.
3. Addition of the binder liquor to the dry mixture and granulate.
4. Dry the granules on a tray in an open air for minimum 4 hours.
5. Drying the compositions in an oven at 37°C for 3 days.

Nile Journal of Basic Science

Volume 3, Number 1, October 2023

Journal Webpage: https://njbs.journals.ekb.eg

Figure 4. Gasless delay composition preparations methods.

Also, the Fabrication of delay element process as the following:

1. Preparation of gasless delay compositions S1, S2, S3…etc.
2. Drying the prepared composition in Vacuum Furnace for 24 hours.
3. Meshing to achieve the required particle size using Mechanical Screening.
4. Loading the composition in Al Tube-Housing.
5. Pressing the loaded compositions using hydraulic pressing system model parker.
6. Assembling initiator Electric Squib (Ignition Source).

3.2 Experimental Apparatus for testing

The burning time testing by Schloder, company testing unites and the thermal analysis qualifications for delay compositions was carried out using (DSC-TAM) apparatus.

Sensitivity test for different stimuli includes (impact, friction, ignition and ESD) have been done. Measurements have been done using the Czechoslovakia (BAM type IN 10455) for impact, BAM friction tester Reichel & Partner GmbHis, heating block tester DT- 400 and SESD 2900 By Schloder for Electrostatic Discharge.

4- Results and Discussion

4.1 Effect of different percentage of fuel (W) on burning rate measurements

Figure (5) represent the effect of different percentage of fuel (W) with respect to oxidizer ($KClO_4$) at constant binder and burning rate modifier ratio on the burning behavior of tungsten delay compositions. The main aspect was the decay of burning rate as the percentage of fuel increase, the dramatic fall in the burning rate was contributed to the decrease of oxygen content in the composition.

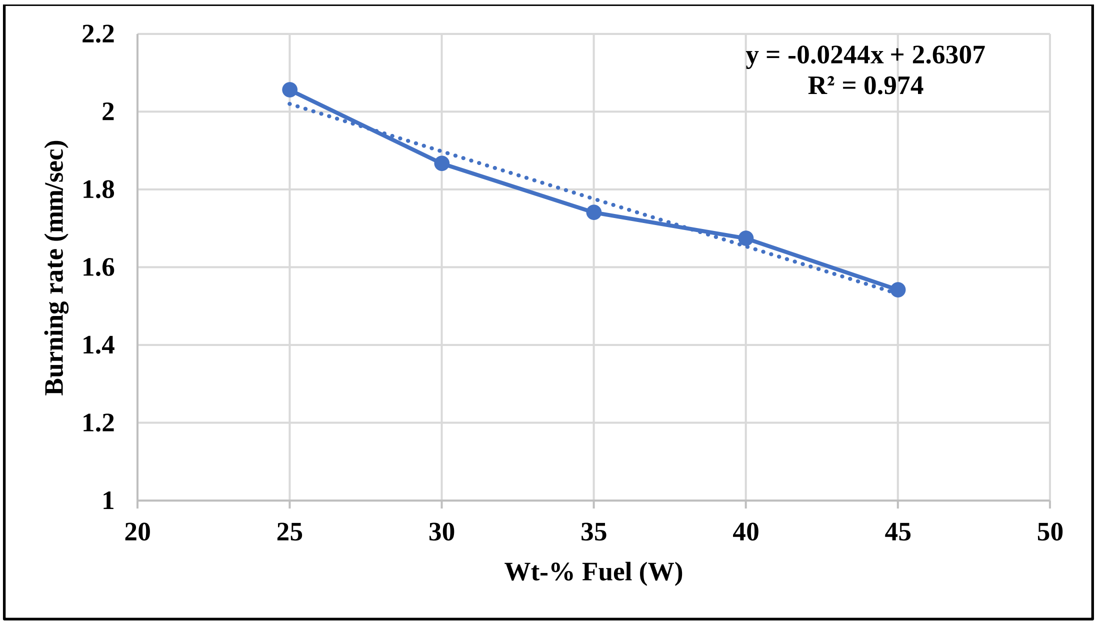

Figure 5. Different percentage of fuel (W) with respect to oxidizer.

Nile Journal of Basic Science

Volume 3, Number 1, October 2023

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A new relation between theoretical heat of formation and measured experimentally burning rate was introduced as clarified in figure (6). This useful relation can be used for estimation the performance parameters of delay compositions.

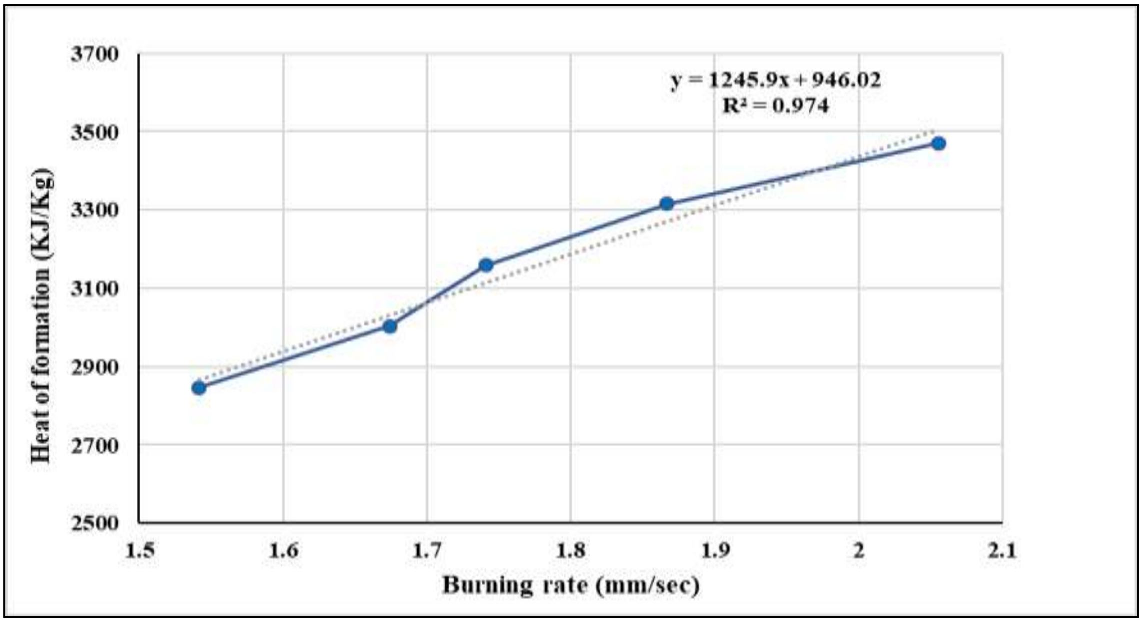

Figure 6. Relation between heat of formation and burning rate.

4.2 Thermal stability test Differential scanning calorimeter (DSC) and TAM

The DSC thermal stability curves, figures (7 - 11) for tungsten delay compositions using 25%, 30%, 35% and 45% tungsten as fuel on the expense of oxidizer ($KClO_4$) shows only an endotherm peak around 306 °C that indicates $KClO_4$ phase transition, no remarks are found for any exothermic DSC features for all tested samples.

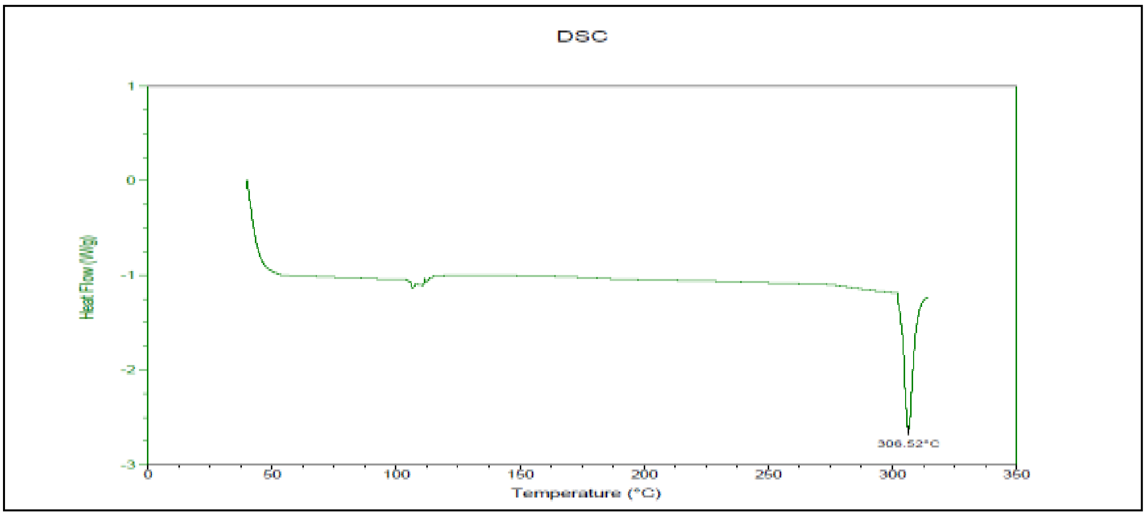

Figure 7. DSC result for delay compositions using 25% (W) as fuel with respect to oxidizer.

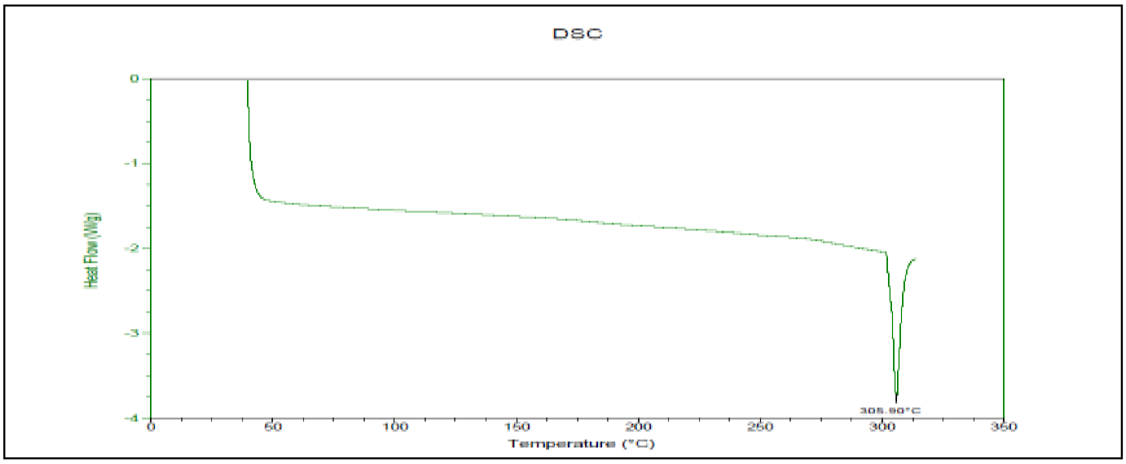

Figure 8. DSC result for delay compositions using 30% (W) as fuel with respect to oxidizer.

Nile Journal of Basic Science

Volume 3, Number 1, October 2023

Journal Webpage: https://njbs.journals.ekb.eg

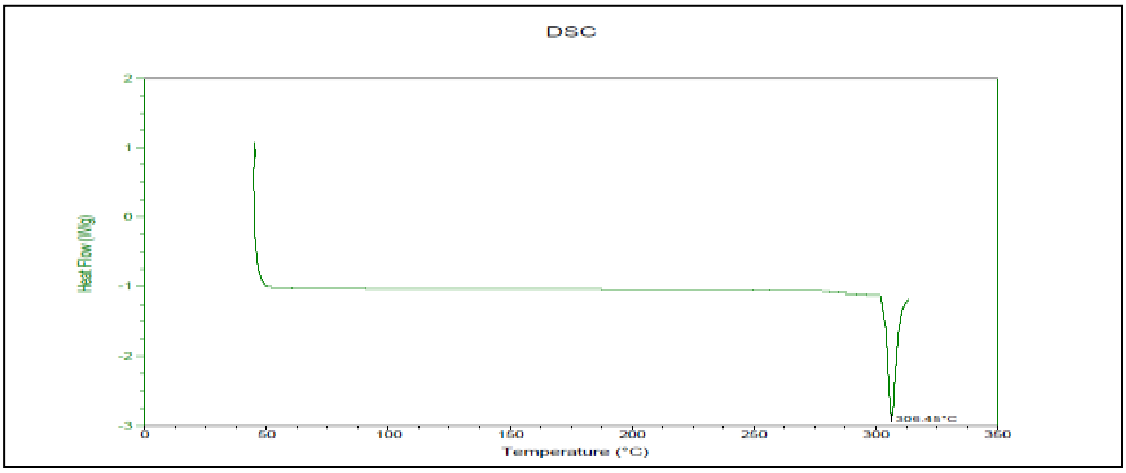

Figure 9. DSC result for delay compositions using 35% (W) as fuel with respect to oxidizer.

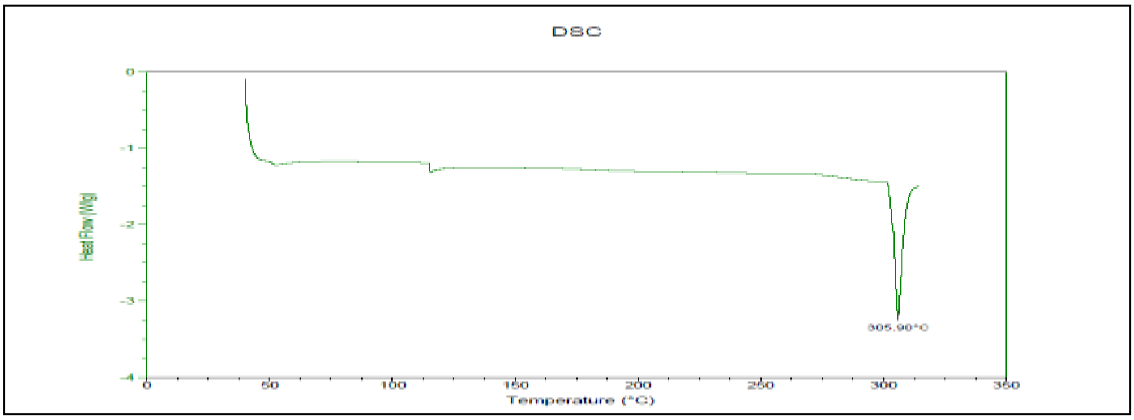

Figure 10. DSC result for delay compositions using 40% (W) as fuel with respect to oxidizer.

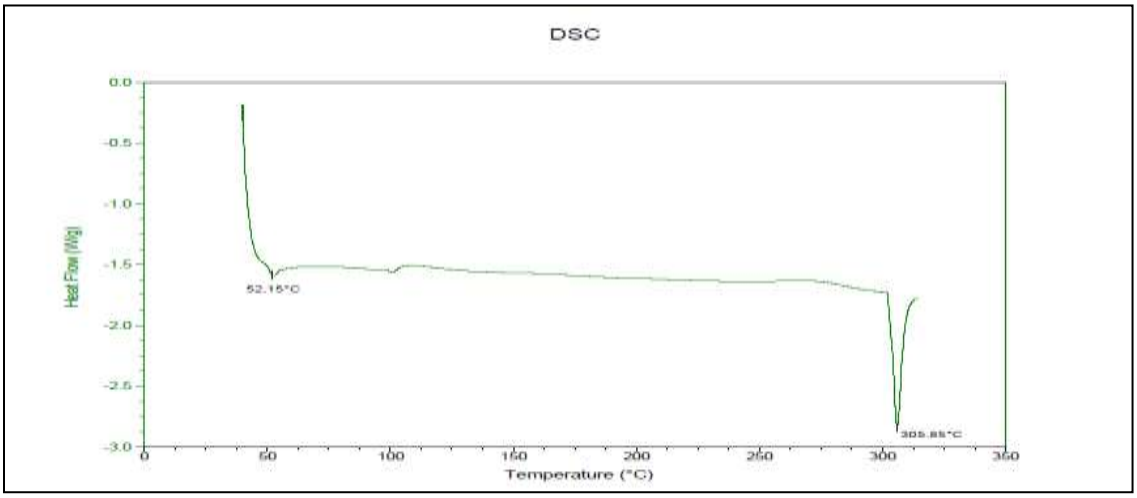

Figure 11. DSC result for delay compositions using 45% (W) as fuel with respect to oxidizer.

The TAM 3 results for the first 3.4 days of micro calorimeter heat release for the tested compositions at 90°C was tabulated. All tested delay samples show fair thermal stability behavior where no heat flow released was observed for all four measurements. Therefore, obtained results give an indication that the compositions will be at stable with chemical and physical state for a period not less than 10 years of storage at ambient temperature 25°C. The TAM 3 results agreed with DSC results that confirm the thermal stability and no decomposition of the analyzed samples.

4. 3. Sensitivity test (Impact-Friction-Ignition-ESD)

According to military standards, used for characterization of pyrotechnic delay compositions the impact sensitivity test was carried out, no sign of sparks or ignition was observed. Friction sensitivity test was conducted according to STANAG 4487, all the results were satisfactory. Electrostatic discharge test according to the standard VG-Norm 95378-11.

No positive evidence for initiation, ignition, spark, noise was observed. Finally, the ignition temperature test was conducted by subjecting the tested samples to temperature up to 400°C with temperature rise 20°C min^{-1}, no ignition reaction was noticed for all tested samples. PVA as a binder is the reason behind these highly thermal and mechanical resistance not only by minimizing the friction energy that cause hot spots, but also by decreasing the rate of heat transfer so preventing any chance for initiation reaction.

5- Conclusion

The theoretical calculation conducted by ICT code for different samples with different percentage of fuel (w) shows decreasing for heat of formation and oxygen balance. The influence of changing the metal fuel percentage produce dramatic decreasing in burning rate which measured experimentally. Gasless delay compositions based on $KClO_4$ as an oxidizer has the advantage of high oxygen content than other oxidizers that sustain a nearly linear burning rate all over the delay element. The novel method which depends on the heat of combustions resulted from ICT thermodynamic equilibrium code has proven to be a valuable tool saving cost, time and effort, for predicting the performance of the gasless delay elements used for rocket propellant systems and rocket assisted projectiles. Thermal analysis tests (DSC, TAM 3) and sensitivity tests such as impact, friction, ignition and ESD were conducted for all the tested delay samples show good stability and safety proprieties during fabrication, handling as well as storage and field operation.

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